NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (4), P. 633–636

TiO_2 based dye-sensitized solar cell using natural dyes

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PACS 88.40.hj, 83.80.Mc, 78.66.Qn **DOI 10.17586/2220-8054-2016-7-4-633-636**

Nanostructured TiO_2 thin films were prepared for various thicknesses on fluorine – doped tin oxide (FTO) conductive glass by the spin coating method. Anthocyanin dye was used to sensitize the sample. The structural characterization was done by XRD. The bandgaps from UV–Vis and photoluminescence measurements are in the range of 2.41 to 2.59 eV. The photocurrent and photovoltage of the cells was measured using Keithley source meter. A maximum conversion efficiency of 0.27 % was observed and the results were discussed.

Keywords: Dye sensitized solar cells, natural dyes, TiO_2 film.

Received: 5 February 2016

Revised: 20 June 2016

1. Introduction

Dye-sensitized solar cells (DSSC) are expected to be used for future clean energy [1, 2] and are usually composed of a dye-capped nanocrystalline porous semiconductor electrode, a metal counter electrode, and a redox electrolyte containing iodide and triiodide ions. The performance of the cell is primarily dependent on the material and quality of the semiconductor electrode and the sensitizer dye used for the fabrication of the cell. In DSSC, the sensitizer (dye) plays a key role in absorbing sunlight and transforming solar energy into electric energy. Numerous metal complexes and organic dyes have been synthesized and utilized as sensitizers. By far, the highest efficiencies for DSSC have been obtained using Ru-containing sensitizer compounds absorbed onto Nano crystalline TiO_2 reached 11–12 % [3, 4]. Although, such DSSC have provided a relatively high efficiency, they are costly, as the resources are limited in quantity. On the other hand, organic dyes are cheaper and are reported to attain efficiencies as high as 9.8 % [5]. The advantages of natural dyes include their easy availability, environmental friendliness and low cost. In this paper, we report the performance of natural anthocyanin, obtained from black rice extraction. This compound would be used as the dye, since anthocyanin has good chemical bonding with titanium dioxide [6].

2. Experimental procedure

The solvent used to extract dye was prepared by using ethanol, acetic acid and distilled water with molarity ratio about 3:2:1. The blackrice was mixed in the solvent, then the mixture was stirred at 50 °C for 30 minutes, the solution formed was filtered by filter paper, to obtain dark-red solution of anthocyanin dye. TiO_2 nanoparticles of 0.2 g is blended using an agate mortar with 0.4 ml nitric acid solution (0.1 M), 0.8 g polyethylene glycol (MW–10,000) and one drop of nonionic surfactant (Triton X–100) to obtain porous TiO_2 film on FTO plate [7]. The blending process was continued using an ultrasonic bath for 30 minutes until it forms thick paste without any clots. A piece of conductive glass (FTO) is selected and placed on a metal sheet. A scotch tape at four sides was used as masking material on the conductive layer restricts the thickness and area of the paste. Then various thicknesses of TiO_2 thin films are coated over FTO plate by spin coating method for various rpm rates (3000, 4000, 5000 and 6000). Later, the plate is sintered at 450 °C for 2 hours under thermal furnace module. The thicknesses of the sample were measured using optical thickness profilometer and the sintered TiO_2 thin films were immersed in natural dyes for 24 hours, allowing the natural dye molecules to be adsorbed onto the surface of TiO_2 nanoparticles. The DSSC photo electrode (TiO_2/anthocyanin) is ready for testing. The samples were characterized by XRD, PL and UV techniques. Finally, the DSSCs were fabricated with platinum as a counter electrode and potassium iodide as liquid electrolyte.

3. Results and discussion

3.1. Structural characterization (XRD)

Various thickness of TiO_2 on FTO plate were deposited using spin coating method and it was found that the thickness of the sample decreases with increased rpm. The XRD patterns of the samples TiO_2 and TiO_2/anthocyanin for various thicknesses are shown in Fig. 1A and 1B respectively. The thickness of the samples was measured using an optical thickness profilometer. In Fig. 1A, the characteristic peaks at 27 °(110), 37 °(301) and 54 °(211) reveal the formation of ructile phase of TiO_2 (JCPDF card No: 73-1765) [8]. The nature of XRD peaks reflect that the nanoparticles are crystalline. Furthermore, the intensity of peak corresponding to (1 1 0) plane decreases with decreased thickness (Fig. 1A). After the absorption of anthocyanin dye, the peak corresponding to the plane (2 2 1) disappears and the peak corresponding to (1 1 0) decreases due to the formation of chemical bonding between TiO_2 and anthocyanin dye molecules (Fig. 1B) [6]. The thickness and XRD parameters are listed in Table 1.

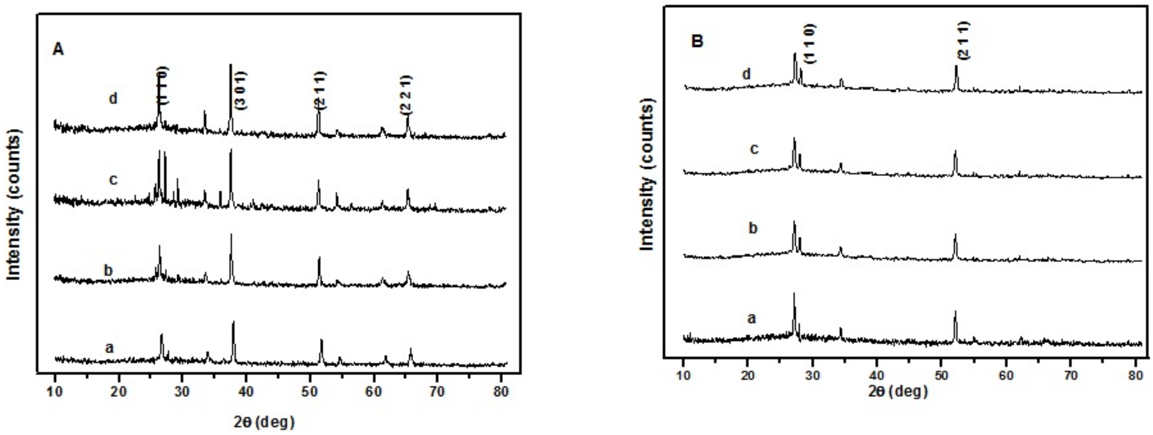

FIG. 1. XRD pattern of the samples prepared at the rpm of a) 3000; b) 4000; c) 5000; d) 6000: A) TiO_2; B) TiO_2/anthocyanin

TABLE 1. Thickness, Lattice Constant, Crystallite size of TiO_2 sample prepared at different rpm

Rotation per minute	Thickness (μm)	Lattice constant (Å)	Crystallite size (nm)
3000	18.62	4.58	27
4000	10.18	4.57	25
5000	7.36	4.56	22
6000	4.78	4.55	21

3.2. Optical measurements

The PL spectra of TiO_2/anthocyanin samples are shown in Fig. 2. The bandgaps, calculated from UV – absorption and Photoluminescence emission spectra of the samples, are given in Table 2. The bandgaps of the prepared samples (2.59 to 2.41 eV) lie in the required range of preparation for solar cells. The intensity of the PL spectra increases with increase in rpm, whereas the bandgaps of the samples decrease due to the decrease in crystallite size [9].

3.3. I–V characterization

The photovoltaic tests of the prepared DSSCs using natural dye extracts as sensitizer were carried out by I–V measurements. Photocurrents and voltages were measured using a Keithley source meter 2400, with a 80 W halogen lamp and AM 1.5 G. The quality of the solar cell is determined by a parameter called solar cell efficiency, which is simply defined by a ratio:

$$\eta = \frac{P_{max}}{P_L} \tag{1}$$

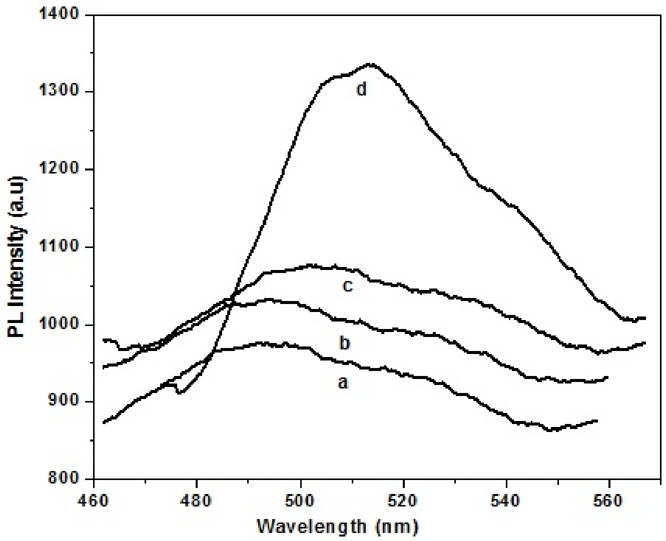

FIG. 2. PL spectra of TiO_2/anthocyanin samples prepared at the rpm of a) 3000; b) 4000; c) 5000; d) 6000

TABLE 2. Bandgap values of TiO_2/anthocyanin samples from PL and UV measurement

Rotation per minute	Band gap (eV)	
	PL	UV
3000	2.57	2.59
4000	2.52	2.52
5000	2.47	2.46
6000	2.41	2.41

where P_{max} is the maximum solar cell power and P_L is power of the incident light. Thus, solar cell efficiency and P_{max} are associated by a linear dependence. The conversion efficiencies were measured and calculated, the results are summarized in Table 3. The fill factor of the sample increases with decrease in thickness of the sample. This increase in fill factor causes increase in efficiency of the DSSCs.

TABLE 3. Conversion Efficiencies of the DSSCs prepared by Natural dyes

Rotation per minute	Thickness (μm)	Fill Factor	Conversion Efficiency (%)
3000	18.62	0.46	0.12
4000	10.18	0.58	0.13
5000	7.36	0.70	0.20
6000	4.78	4.28	0.27

4. Conclusion

The synthesized nanostructured porous TiO_2 samples were sensitized using anthocyanin dye. The structural characterization was done by XRD. The XRD pictures showed the features of TiO_2 and the effect of anthocyanin dye (blackrice). The bandgaps calculated from the UV absorption spectrum are in the range 2.41 to 2.59 eV, which is in agreement with PL measurements. The bandgap decreases with increased RPM's. The suitability of these samples for solar cell applications and sensors were studied and the samples were optimized using UV absorption. The DSSC prepared at the ratio 6000 rpm showed the highest efficiency of 0.27 %.

References

[1] Grätzel M. Dye-sensitized Solar cells. *J. Photochem. Photobiol., C. Photochem. Rev.*, 2003, **4**, P. 145–153.

[2] Law M., Greene L.E., Johnson J.C., Saykally R., Yang P. Nanowire dye-sensitized solar cells. *Nat. Mater.*, 2005, **4,** P. 455–459.

[3] Chiba Y., Islam A., Watanabe Y., Komiya R., Koide N., Han L.Y. Dye-Sensitized Solar Cells with Conversion Efficiency of 11.1%. *Jpn. J. Appl. Phys.*, 2006, **45**, P. L638–L640.

[4] Buscaino R., Baiocchi C., Barolo C., Medana C., Grätzel M., Nazeeruddin Md.K., Viscardi G. A mass spectrometric analysis of sensitizer solution used for dye-sensitized solar cell. *Inorg. Chim. Acta*, 2008, **361**, P. 798–805.

[5] Zhang G., Bala H., Cheng Y., Shi D., Lv X., Yu Q., Wang P. High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary π-conjugated spacer. *Chem. Commun.*, 2009, P. 2198–2200.

[6] Hao S., Wu J., Huang Y., Lin J. Natural dyes as photosensitizers for dye-sensitized solar cell. *Solar Energy*, 2006, **80**(2), P. 209–216.

[7] Kim S., Lee J.K., Kang S.O., Ko J.J., Yum J.H., Fantacci S., De Angelis F., DiCenso D., Nazeeruddin Md.K., Grätzel M. Molecular Engineering of Organic Sensitizers for Solar Cell Applications. *Journal of American Chemical Society*, 2006, **128**, P. 16701–16707.

[8] Sanjay Chakane, Anisha Gokarna, Bhoraskar S.V. Metallophthalocyanine coated porous silicon gas sensor selective to NO_2. *J.Sensors and Actuators B*, 2003, **92**, P. 1–5.

[9] Azim-Araghi M.E., Karimi-Kerdabadi E., Jafari M.J. *Eur. Phys. J. Appl. Phys.*, 2011, **55**, P. 302–303.